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| (51) International Patent Classification 6 : H01M 6/14, 6/18, 4/60 | A1 | (11) International Publication Number: WO 98/00877 (43) International Publication Date: 8 January 1998 (08.01.98) |
| (21) International Application Number: PCT/US97/04975 | | (81) Designated States: AU, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). |
| (22) International Filing Date: 25 March 1997 (25.03.97) | | |
| (30) Priority Data: 08/674,563 2 July 1996 (02.07.96) US | | Published <i>With international search report.</i> |
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| (54) Title: PREPARATION AND USE OF THIN FLEXIBLE CATHODES IN ALKALI METAL ELECTROCHEMICAL CELLS | | |
| (57) Abstract | | |
| A method of forming flexible electrodes, preferably cathodes, is described. The method involves casting a slurry of an electrode active material, preferably mixed with a binder material and a conductive diluent, to a conductive substrate followed by pressing the laminate. The conductive substrate can be roughened or etched using an acid solution, or the substrate can be used in a cleaned but untreated condition. The thusly produced cathodes are useful for discharge in alkali metal, nonaqueous electrochemical cells. | | |
| <p>The graph plots Voltage (VOLTS) on the y-axis (1 to 4) against Capacity (Ah) on the x-axis (0.0 to 0.4). Three curves are shown: curve 40 starts at ~3.2V and ends at ~2.0V; curve 42 starts at ~2.6V and ends at ~2.0V; curve 44 starts at ~2.4V and ends at ~2.0V. All curves show a slight initial increase in voltage before decreasing.</p> | | |

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PREPARATION AND USE OF THIN FLEXIBLE
CATHODES IN ALKALI METAL ELECTROCHEMICAL CELLS

BACKGROUND OF THE INVENTION

1. Field of the Invention

5 The present invention generally relates to the conversion of chemical energy to electrical energy, and more particularly, to an alkali metal electrochemical cell having an electrode formed by casting a slurry of electrode active material to a metal foil followed by
10 pressing the laminate. The resulting electrode active component is thinner than conventional pressed powder electrodes while maintaining acceptable flexibility characteristics. Thinner electrodes benefit electrode surface area which in turn results in increased
15 discharge capacity.

2. Prior Art

Various patents disclose metals, metal oxides,
20 mixed metal oxides and metal sulfides as active materials for use in electrochemical cells having increased energy density and which are capable of delivering the high current pulses required for powering implantable medical devices. Such materials include
25 silver vanadium oxide and copper silver vanadium oxide and are described by U.S. Patent Nos. 4,310,609 to Liang et al.; 4,830,940 to Keister et al.; 5,389,472 to Takeuchi et al.; 5,472,810 to Takeuchi et al. and 5,498,494 to Takeuchi et al. These patents are all
30 assigned to the assignee of the present invention and incorporated herein by reference.

The anhydrous, dry powder form of the active materials described in these prior art patents are typically mixed with a conductive diluent and a binder

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material, and layers of the dry powder active mixture are pressed onto opposed sides of a conductive, current collector screen. It is believed that the resulting electrode maintains its mechanical integrity during
5 manufacture into various cell configurations by the active mixture locking to itself through the screen perforations. However, pressed powder electrodes of the prior art have limited, if any, flexibility and are generally incapable of being formed at thickness less
10 than approximately 0.013 inches.

To further enhance the energy density of cells comprising the above discussed active materials and others, there is a need for flexible electrodes having improved thickness characteristics i.e., electrodes
15 which are thinner than those generally known by the prior art, but which have increased current capacity. Flexibility is important for shaping or forming the electrodes into various cell configurations such as the jellyroll configuration. However, flexibility must not
20 be improved at the expense of mechanical integrity. Improved electrode thickness characteristics result in an increased electrode surface area for a given volume casing which is believed to increase the current capacity of cells incorporating the electrodes.

25

SUMMARY OF THE INVENTION

The present invention is directed to a thin, flexible electrode comprising an electrode active
30 material contacted to a conductive substrate serving as the current collector. The present invention is also directed to a method of manufacturing such an electrode. The thusly formed electrode is preferably a cathode for use in an alkali metal, organic electrolyte cell. The
35 preferred conductive substrate is comprised of an aluminum or aluminum alloy in the form of a screen or a

foil. In the latter case, the foil can be roughened or etched using an acid solution, or the foil can be used in a cleaned but untreated condition. To provide an electrode, electrode active material preferably

- 5 including a conductive diluent and a binder material is first formed into a slurry by mixing with a solvent, and then the active slurry is cast or otherwise contacted to the conductive substrate, followed by pressing.

These and other aspects of the present invention
10 will become more apparent to those skilled in the art by reference to the following description and to the appended drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

15

Fig. 1 is a photograph showing the surface condition of an untreated aluminum alloy substrate.

Fig. 2 is a photograph showing the surface condition of an aluminum alloy substrate similar to that
20 shown in Fig. 1 but after treatment in the sulfuric acid solution according to the present invention.

Fig. 3 is a graph showing the voltage under background load and p1 minima and p4 minima pulse train voltages versus amp hours of a cell having a cathode
25 comprising a silver vanadium oxide admixture slurry cast and pressed to a surface treated aluminum substrate.

Fig. 4 is a graph showing the voltage versus amp hours of a cell having a cathode comprising a silver vanadium oxide admixture slurry cast and pressed to a
30 surface treated conductive substrate and subjected to pulses 1.5 A in amplitude.

Fig. 5 is a graph showing the voltage versus amp hours of a cell having a cathode comprising a silver vanadium oxide admixture slurry cast and pressed to a
35 surface treated conductive substrate and subjected to pulses 2.0 A in amplitude.

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Fig. 6 is a graph showing the average voltage versus amp hours of five cells similar to those discharged to construct Figs. 4 and 5.

5 Fig. 7 to 9 are graphs showing the voltage versus amp hours of cells having a cathode comprising a silver vanadium oxide admixture slurry cast and pressed to a surface treated conductive substrate and subjected to pulses 1.5 A, 1.75 A and 2.0 A in amplitude, respectively.

10 Fig. 10 is a graph showing the voltage versus amp hours of a cell having a cathode comprising a silver vanadium oxide admixture slurry cast and pressed to an untreated aluminum substrate.

15 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The electrochemical cell of the present invention comprises an anode of a metal selected from Group IA of the Periodic Table of the Elements, including lithium, 20 sodium, potassium, etc., and their alloys and intermetallic compounds including, for example, Li-Si, Li-Al, Li-B and Li-Si-B alloys and intermetallic compounds. The preferred anode comprises lithium, and the more preferred anode comprises a lithium alloy such 25 as a lithium-aluminum alloy. However, the greater the amount of aluminum present by weight in the alloy the lower the energy density of the cell.

The form of the anode may vary, but preferably the anode is a thin metal sheet or foil of the anode metal, 30 pressed or rolled on a metallic anode current collector, i.e., preferably comprising nickel, to form an anode component. In the exemplary cell of the present invention, the anode component has an extended tab or lead of the same material as the anode current 35 collector, i.e., preferably nickel, integrally formed therewith such as by welding and contacted by a weld to

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a cell case of conductive metal in a case-negative electrical configuration. Alternatively, the anode may be formed in some other geometry, such as a bobbin shape, cylinder or pellet to allow an alternate low 5 surface cell design.

The electrochemical reaction at the cathode involves conversion of ions which migrate from the anode to the cathode in atomic or molecular forms. The solid cathode material may comprise a metal element, a metal 10 oxide, a mixed metal oxide and a metal sulfide, and combinations thereof. The metal oxide or the mixed metal oxide can be formed by the chemical addition, reaction, or otherwise intimate contact of various metal oxides and/or metal elements, preferably during thermal 15 treatment, sol-gel formation, chemical vapor deposition or hydrothermal synthesis in mixed states. The active materials thereby produced contain metals, oxides and sulfides of Groups IB, IIB, IIIB, IVB, VB, VIB, VIIB and VIII which includes the noble metals and/or other oxide 20 and sulfide compounds.

According to one aspect of the present invention, readily decomposable compounds consisting of metals from Groups IB, IIB, IIIB, IVB, VB, VIB, VIIB, as well as similarly decomposable compounds from Group VIII, are 25 thermally treated so as to effect the rapid preparation of the oxides or the respective metal elements themselves to be utilized further in the preparation of suitable cathode materials. Such readily decomposable materials include, but are not limited to, those classes 30 of compounds known as nitrates, nitrites, carbonates and/or ammonium salts. The precursor materials (i.e., nitrates, nitrites, carbonates, ammonium compounds, etc.) may be decomposed in a combined state or individually decomposed and thereafter combined in an 35 oxide/decomposable metal salt compound and subsequently decomposed to form the cathode active material

comprising a mixed metal oxide. Preferred mixed metal oxides are prepared by thermally decomposing a vanadium salt, suitably ammonium meta-vanadate to produce vanadium pentoxide. A decomposable metal salt, suitably
5 the nitrates of a second metal and possibly a third metal, are then added to the vanadium pentoxide, thoroughly mixed therewith and thereafter thermally treated. The second and third metals are most preferably silver and copper.

10 One preferred mixed metal oxide has the general formula $SM_xV_2O_y$, wherein SM is a metal selected from the Groups IB to VIIIB and VIII of the Periodic Table of elements and x is about 0.30 to 2.0 and y is about 4.5 to 6.0 in the general formula. By way of illustration,
15 and in no way intended to be limiting, one exemplary cathode active material comprises silver vanadium oxide (SVO) having the general formula $Ag_xV_2O_y$, in any one of its many phases, i.e., β -phase silver vanadium oxide having in the general formula x = 0.35 and y = 5.8, γ -phase
20 silver vanadium oxide having in the general formula x = 0.74 and y = 5.37 and ϵ -phase silver vanadium oxide having in the general formula x = 1.0 and y = 5.5, and combinations and mixtures of phases thereof.

25 Another preferred composite cathode material includes V_2O_z wherein z ≤ 5 combined with Ag_2O_z wherein z=0 to 1 and CuO_z wherein z=0 to 1 to provide the mixed metal oxide having the general formula $Cu_xAg_yV_2O_z$, (CSVO). Thus, this composite cathode active material may be
30 described as a metal oxide-metal oxide-metal oxide, a metal-metal oxide-metal oxide, or a metal-metal-metal oxide and the range of material composition found for $Cu_xAg_yV_2O_z$ is preferably about $0.01 \leq x \leq 1.0$, about $0.01 \leq y \leq 1.0$ and about $5.01 \leq z \leq 6.5$. Typical forms of
35 CSVO are $Cu_{0.16}Ag_{0.67}V_2O_5$ with z being about 5.5 and $Cu_{0.5}Ag_{0.5}V_2O_5$ with z being about 5.75. The oxygen content

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is designated by z since the exact stoichiometric proportion of oxygen in CSVO can vary depending on whether the cathode material is prepared in an oxidizing atmosphere such as air or oxygen, or in an inert 5 atmosphere such as argon, nitrogen and helium.

Additional cathode active materials include manganese dioxide, lithium cobalt oxide, lithium nickel oxide, copper oxide, titanium disulfide, copper sulfide, iron sulfide, iron disulfide, copper vanadium oxide, and 10 mixtures thereof. The cathode active material is preferably present in the cathode at about 80 to 99 weight percent.

The above described active materials are formed into an electrode for incorporation into an 15 electrochemical cell by mixing one or more of them with up to about 5 weight percent of a conductive additive such as acetylene black, carbon black and/or graphite. A preferred carbonaceous diluent is Ketjenblack carbon. Metallic powders such as nickel, aluminum, titanium and 20 stainless steel in powder form are also useful as conductive diluents when mixed with the above listed active materials. The electrode further comprises up to about 10 weight percent of a binder material which is preferably a fluoro-resin powder such as powdered 25 polytetrafluoroethylene (PTFE) or powdered polyvinylidene fluoride (PVDF). More specifically, a preferred cathode active admixture comprises, by weight, about 94% SVO in any one of its many phases, or mixtures thereof, and/or CSVO mixed with about 3 weight percent 30 of a binder material and about 3 weight percent of a conductive diluent.

According to the present invention, the thusly formed electrode active admixture is converted into a slurry by mixing with a high permittivity solvent such 35 as a cyclic amide, a cyclic carbonate or a cyclic ester. Suitable high permittivity solvents include propylene

carbonate, ethylene carbonate, γ -butyrolactone, N-methyl-pyrrolidinone, dimethyl sulfoxide, acetonitrile, dimethyl formamide and dimethyl acetamide, and mixtures thereof.

5 The active slurry is then cast or otherwise applied or contacted to a conductive foil substrate which serves as the current collector for the electrode. Suitable materials for the current collector substrate include nickel, aluminum, stainless steel, mild steel and
10 titanium with aluminum being preferred. According to one embodiment of the present invention, prior to being contacted with the active slurry the foil is roughened to increase its surface area by immersion in an acidic etchant solution such as a sulfuric acid solution. A
15 preferred etchant solution is designated a P2 solution and comprises sulfuric acid (H_2SO_4) having ferrous sulfate ($Fe_2(SO_4)_3 \cdot 5H_2O$) dissolved therein. If surface roughening is desired, the foil is immersed in the sulfuric acid solution for about 8 to 12 minutes at
20 about 50°C to 70°C to provide the substrate with a pitted or honeycombed surface texture. On the other hand, if the surface roughening is not desired, the foil substrate is preferably cleaned of surface contamination such as dirt, grease, oil and the like and then used in
25 its cleaned but untreated condition. After drying to remove all residual water from the slurry, contacted to the conductive substrate, the resulting anhydrous active admixture is calendared under a pressure of about 40 tons/inch² to laminate the active admixture to either the etched or unetched current collector foil, as the case may be, to thereby form the electrode according to the present invention. Furthermore, if desired the substrate can be a screen comprised of one or more of the enumerated conductive materials.
30
35 Cathodes prepared as described above are flexible and may be in the form of one or more plates operatively

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associated with at least one or more plates of anode material, or in the form of a strip wound with a corresponding strip of anode material in a structure similar to a "jellyroll".

5 As previously discussed in the Prior Art section, conventional electrodes fabricated from dry powder active mixtures pressed onto a perforated conductive screen generally are limited to total thicknesses not less than 0.013 inches (measured electrode thickness
10 includes the first and second active layers or plates pressed onto the opposed sides of the intermediate conductive screen). In the present invention, the electrode comprising the active admixture cast and pressed onto the opposed sides of the conductive foil
15 ranges between about 0.002 to 0.009 inches. The conductive foil itself typically is 0.001 inches thick which means that castings as thin as 0.0005 inches can be applied or contacted to the foil without compromising mechanical integrity. Decreasing electrode thickness
20 beneficially increases electrode surface area which in turn benefits discharge current capacity.

In order to prevent internal short circuit conditions, the cathode is separated from the Group IA anode material by a suitable separator material. The separator is of electrically insulative material, and the separator material also is chemically unreactive with the anode and cathode active materials and both chemically unreactive with and insoluble in the electrolyte. In addition, the separator material has a degree of porosity sufficient to allow flow therethrough of the electrolyte during the electrochemical reaction of the electrochemical cell. Illustrative separator materials include fabrics woven from fluoropolymeric fibers including polyvinylidene fluoride,
30 polyethylenetetrafluoroethylene, and
35 polyethylenechlorotrifluoroethylene used either alone or

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laminated with a fluoropolymeric microporous film, non-woven glass, polypropylene, polyethylene, glass fiber materials, ceramics, polytetrafluoroethylene membrane commercially available under the designation ZITEX

5 (Chemplast Inc.), polypropylene membrane commercially available under the designation CELGARD (Celanese Plastic Company, Inc.) and a member commercially available under the designation DEXIGLAS (C.H. Dexter, Div., Dexter Corp.).

10 The electrochemical cell of the present invention further includes a nonaqueous, ionically conductive electrolyte which serves as a medium for migration of ions between the anode and the cathode electrodes during the electrochemical reactions of the cell. The

15 electrochemical reaction at the electrodes involves conversion of ions in atomic or molecular forms which migrate from the anode to the cathode. Thus, nonaqueous electrolytes suitable for the present invention are substantially inert to the anode and cathode materials, 20 and they exhibit those physical properties necessary for ionic transport, namely, low viscosity, low surface tension and wettability.

A suitable electrolyte has an inorganic, ionically conductive salt dissolved in a nonaqueous solvent, and 25 more preferably, the electrolyte includes an ionizable alkali metal salt dissolved in a mixture of aprotic organic solvents comprising a low viscosity solvent and a high permittivity solvent. The inorganic, ionically conductive salt serves as the vehicle for migration of 30 the anode ions to intercalate into the cathode active material, and has the general formula $MM'F_6$ or $MM'F_4$ wherein M is an alkali metal similar to the alkali metal comprising the anode and M' is an element selected from the group consisting of phosphorous, arsenic, antimony 35 and boron. Examples of salts yielding $M'F_6$ are: hexafluorophosphate (PF_6), hexafluoroarsenate (AsF_6) and

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hexafluoroantimonate (SbF_6) while tetrafluoroborate (BF_4) is exemplary of salts yielding $M'F_4$. Thus, in the case of the anode comprising lithium, the alkali metal salt comprises lithium hexafluorophosphate, lithium
5 hexafluoroarsenate, lithium hexafluoroantimonate or lithium tetrafluoroborate dissolved in a suitable solvent mixture. Alternatively, the corresponding sodium or potassium salts may be used. Other inorganic salts useful with the present invention include $LiClO_4$,
10 $LiAlCl_4$, $LiGaCl_4$, $LiC(SO_2CF_3)_3$, $LiN(SO_2CF_3)_2$, $LiSO_3F$, $LiB(C_6H_5)_4$ and $LiCF_3SO_3$, and mixtures thereof.

Low viscosity solvents include tetrahydrofuran (THF), methyl acetate (MA), diglyme, triglyme, tetraglyme, dimethyl carbonate (DMC), diethyl carbonate,
15 1,2-dimethoxyethane (DME) and mixtures thereof, and high permittivity solvents include cyclic carbonates, cyclic esters and cyclic amides such as propylene carbonate (PC), ethylene carbonate (EC), acetonitrile, dimethyl sulfoxide, dimethyl formamide, dimethyl acetamide,
20 γ -butyrolactone (GBL) and N-methyl-pyrrolidinone (NMP) and mixtures thereof. In the present invention, the anode is preferably lithium metal and the preferred electrolyte is 1.0M to 1.4M $LiAsF_6$ dissolved in an aprotic solvent mixture comprising a 50/50 mixture (by volume) of propylene carbonate (PC) and dimethoxyethane (DME).
25

The preferred form of the electrochemical cell is a case-negative design wherein the anode/cathode couple is inserted into a conductive metal casing such that the
30 casing is connected to the anode current collector in a case-negative configuration, as is well known to those skilled in the art. A preferred material for the casing is titanium although stainless steel, mild steel, nickel-plated mild steel and aluminum are also suitable.
35 The casing header comprises a metallic lid having an opening to accommodate the glass-to-metal seal/terminal

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pin feedthrough for the cathode electrode. The anode electrode is preferably connected to the case or the lid. An additional opening is provided for electrolyte filling. The casing header comprises elements having
5 compatibility with the other components of the electrochemical cell and is resistant to corrosion. The cell is thereafter filled with the electrolyte solution described hereinabove and hermetically sealed such as by close-welding a stainless steel plug over the fill hole,
10 but not limited thereto. The cell of the present invention can also be constructed in a case-positive design.

The following examples describe the manner and process of manufacturing an electrochemical cell
15 according to the present invention, and they set forth the best mode contemplated by the inventors of carrying out the invention, but they are not to be construed as limiting.

EXAMPLE I

Silver vanadium oxide (SVO) was sieved to remove particles larger than 0.007 inches. 4.25 grams of the 5 resulting SVO, 0.15 grams of Ketjenblack carbon and 0.10 grams of graphite #38 powder were mixed using a mortar and pestle. The resulting admixture was added to 2.87 grams of a 17.3 wt% solution of Kynar 711 polyvinylidene fluoride in dimethyl formamide (DMF) and made less 10 viscous with 14 ml of additional DMF.

Aluminum alloy foil designated as 1145-0 was etched using a sulfuric acid solution designated as a P2 solution which was made by bringing 210 ml of concentrated sulfuric acid (H_2SO_4) and 183.76 grams of 15 ferrous sulfate ($Fe_2(SO_4)_3 \cdot 5H_2O$) to 1 liter with water. The aluminum was immersed for 10 minutes in the etchant solution held at 60°C, then washed in deionized water and air dried. This treatment produced a honeycombed or pitted pattern on the aluminum surface. Figs. 1 and 2 20 show 1000x magnification scanning electron microscope photos of untreated and P2 etched 1145-0 aluminum alloy foil, respectively.

The SVO slurry was shaken and transferred using a scoopula to the etched aluminum foil. The slurry was 25 spread using a doctor blade with a gap of 0.008 inches to provide a uniform coating thereon. The casting was allowed to dry in a flowing air hood overnight before a coupon of $5.2cm^2$ was cut from the laminate. Drying generally reduces the thickness of the active mixture by 30 about one-half. In this example, the dried active casting had a thickness of about 0.004 inches. A 0.125 x 0.125 inch area was cleared from one corner of the coupon before it was pressed at 6.15 tons/cm². Pressing further reduced the thickness of the active casting to 35 about 0.0015 to 0.002 inches.

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A 0.125 x 6 inch aluminum lead was resistance spot welded to the cleared area of the coupon. The cathode laminate was wrapped in two layers of CELGARD 4560 polypropylene separator material, and a piece of lithium metal of a similar dimension was placed against the SVO coated side of the cathode followed by a screen with a lead to serve as the current collector for the lithium anode. The electrode assembly was held together between glass slides using a metal clip and positioned in a glass vessel of suitable dimension with the leads allowed to hang over the rim of the vessel. The vessel was filled with 1M LiAsF₆ in 1:1, by volume, propylene carbonate and dimethoxyethane. A rubber stopper provided a lid for the vessel. The cell was discharged under semi-hourly applied pulse trains comprising four, 10 second, 0.094 A (18 mA/cm²) pulses with 15 seconds rest between each pulse. A plot of the open circuit voltage prior to each pulse train application, the minimum voltage during the first pulse (p1 minima) of each train and the minimum voltage during the fourth pulse (p4 minima) of each train is presented in Fig. 3. Specifically, Fig. 3 is a graph showing the discharge of the above described cell constructed in this example according to the present invention, wherein curve 30 was constructed from the prepulse voltage and curves 32 and 34 were constructed from the P1 Min. and P4 Min. discharge voltages versus delivered capacity, respectively.

The cell delivered 0.028 Ah to a 2.0 V cutoff as defined by a pulse four minimum at or below 2.0 V.

EXAMPLE II

Silver vanadium oxide was ball milled for 2 hours using 1/2 x 1/2 inch cylindrical ceramic media in a polytetrafluoroethylene jar. This material was then

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baked at 375°C for 65 hours prior to being sieved to remove particles larger than 0.0041 inches. 47 grams of the resulting sample of SVO was mixed with 1.5 grams of Ketjenblack carbon (3% by weight) using a mortar and 5 pestle. The resulting admixture was added to 7.5 grams of a 17.3 wt% solution of Kynar 711 polyvinylidene fluoride in dimethyl formamide and made less viscous with about 45 ml of additional DMF.

This cathode active mixture was spread on one side 10 of a P2 etched 1145-0 aluminum foil using a doctor blade having a gap of about 0.008 inches, and allowed to dry to a thickness of about 0.004 inches, as described in Example I. The second side of the aluminum foil was then coated in a similar manner to provide samples 15 comprising the SVO cathode active material contacted to both sides of the P2 surface treated foil collector. The samples were about 5 x 12 inches. From these large samples, smaller ribbons were cut to 0.695 inches in width. Cathodes of 13.25 inches in length were 20 fabricated from smaller pieces by clearing areas of 0.125 inches from the ribbon ends, pressing the pieces at 6.15 tons/cm² and resistance spot welding the pieces together. Pressing compacted the active material to a thickness of about 0.0015 to 0.002 inches on each side 25 of the aluminum foil. Leads were welded to the cathodes in the cleared areas. Lead placement was at positions about one-quarter of the total length of the cathode from each of its ends.

To test the mechanical integrity of the pressed 30 ribbons, several ribbons were manipulated into S-shaped configurations. Those folds forming a trough placed the pressed active material under compression forces while the folds forming ridges subjected the active press to tension forces. In either case, it was noted that the 35 active material remained contacted to the conductive foil and that no sloughing or cracking was present.

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Anodes of 14.25 x 0.605 x 0.008 inches were
fabricated by applying 0.0012 thick lithium to a 0.580
inch thick expanded nickel metal screen. The anodes had
leads at one end and at a position about 3/4 along their
5 lengths.

Both the anodes and the cathodes were wrapped in
one layer of CELGARD 2400 polypropylene separator before
being wound together in a jellyroll configuration and
placed in a stainless steel vessel of 0.551 x 0.708 x
10 0.998 inch dimension. The anode leads were welded to
the side of the vessel and the cathode leads were welded
to a glass-to-metal hermetic feedthrough in the vessel
lid. The cells were then activated with an electrolyte
of 1 M LiAsF₆ in 1:1, by volume, propylene carbonate and
15 dimethoxyethane. Open circuit voltages of the cells
were 3.45 to 3.47 V. Thirty cells were made.

All testing was performed at 37°C. The cells were
discharged under loads of 20kΩ for 20 hours followed by
one week at open circuit storage. Pulse trains
20 comprising four, 10 second, 1.5 A (13 mA/cm²) pulses with
15 seconds rest between each pulse were applied to each
cell. The average last load voltage under the 20kΩ
load, open circuit voltage prior to the pulse train
application, the minimum voltage during the first pulse
25 of each train, the voltage at the end of the first pulse
of each train and the minimum voltage during the fourth
pulse of the train for the thirty cells constructed in
this example are presented in Table 1.

30

TABLE 1

| | |
|--------------|-------|
| last load, V | 3.203 |
| prepulse, V | 3.258 |
| p1 min, V | 2.311 |
| p1 last | 2.318 |
| 35 p4 min | 2.358 |

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EXAMPLE III

Nine of the cells constructed in Example II were pulse discharged by applying to each cell a pulse train comprising four, 10 second 1.5 A (14 mA/cm^2) pulses with 5 15 seconds rest between each pulse every thirty minutes. A typical discharge curve is shown in Fig. 4. Particularly, Fig. 4 is a graph showing the discharge of a typical one of these nine cells wherein curve 40 was constructed from the prepulse voltage and curves 42 and 10 44 were constructed from the P1 Min. and P4 Min. discharge voltages versus delivered capacity, respectively.

Nine additional cells of those constructed in Example II were pulse discharged by applying to each 15 cell a pulse train comprising four, 10 second, 2.0 A (18 mA/cm^2) pulses with 15 seconds rest between each pulse every thirty minutes. A typical discharge curve is shown in Fig. 5. Specifically, Fig. 5 is a graph 20 showing the discharge of a typical one of these nine cells wherein curve 50 was constructed from the prepulse voltage and curves 52 and 54 were constructed from the P1 Min. and P4 Min. discharge voltages versus delivered capacity, respectively.

The average capacity delivered by each group of 25 nine cells to specified cutoffs is presented in Table 2.

TABLE 2

| | Ah to 2.0 V | Ah to 1.7 V | Ah to 1.5 V |
|-----------------|-------------|-------------|-------------|
| 30 1.5 A trains | 224 | 253 | 264 |
| 2.0 A trains | 224 | 255 | 268 |

The remaining twelve cells constructed in Example II were discharged under loads of $73.2 \text{ k}\Omega$. Every eight 35 weeks these cells were subjected to a pulse train comprising four, 10 second, 1.5 A (14 mA/cm^2) pulses with

15 seconds rest between each pulse. The average voltage prior to the pulse train application, the minimum voltage during the first pulse of each train, and the minimum voltage during the fourth pulse of the train are
5 presented graphically in Fig. 6 for a sampling of five of these cells. Particularly, Fig. 6 is a graph showing the average discharge of five of these cells wherein curve 60 was constructed from the average prepulse voltage and curves 62 and 64 were constructed from the
10 average P1 Min. and P4 Min. discharge voltages versus delivered capacity, respectively.

EXAMPLE IV

15 Silver vanadium oxide was attrited for 1 hour using 1/4 inch spherical steel media to reduce its average particle size. 9 grams of the resulting ground SVO was mixed with 0.5 grams of Ketjenblack carbon (5% by weight) using a mortar and pestle. The resulting
20 admixture was added to 2.86 grams of a 17.3 wt % solution of Kynar 711 polyvinylidene fluoride in dimethyl formamide and made less viscous by the addition of more DMF.

This cathode active admixture was spread on one
25 side of a P2 etched 1145-0 aluminum foil (0.008 inches in thickness) and dried to a thickness of about 0.004 inches thick, as described in Example I. The second side of the aluminum foil was then coated in a similar manner so that a sample having both sides coated
30 resulted. The sample was about 5 x 12 inches. From this large sample, smaller ribbons were cut to 0.695 inches in width. Cathodes of 15.5 inches in length were fabricated from smaller pieces by clearing areas of 0.125 inches from the ribbon ends, pressing the pieces
35 at 6.15 tons/cm² to a thickness of about 0.0015 to 0.002 inches, and resistance spot welding the pieces together.

Leads were welded to the cathodes in the cleared areas. Lead placement was at positions about one-quarter of the total length of the cathode from each of its ends.

Anodes of 16.5 x 0.605 x 0.008 inches were
5 fabricated by applying 0.0012 thick lithium to a 0.580 inch thick expanded nickel metal screen. The anodes had leads at one end and at a position about 3/4 along their lengths.

Both the anodes and the cathodes were wrapped in
10 one layer of CELGARD 2400 separator before being wound together in a jellyroll configuration and placed in a stainless steel vessel of 0.551 x 0.708 x 0.998 inch dimension. The anode leads were welded to the side of the vessel and the cathode leads were welded to a glass-to-metal hermetic feedthrough in the vessel lid.

15 Nineteen cells were constructed in this manner and activated with an electrolyte of 1M LiAsF₆ in 1:1, by volume, propylene carbonate and dimethoxyethane. Open circuit voltages of the cells were 3.45 to 3.47 V.

20 All testing was performed at 37°C. Each of the cells was burned-in by discharge under a load of 20 kΩ for 20 hours. Three of the cells were then pulse discharged by applying to each cell a pulse train comprising four, 10 second pulses with 15 seconds rest
25 between each pulse every thirty minutes. Pulse amplitudes of either 1.5 A, 1.75 A or 2.0 A were used. Discharge curves are shown in Figs. 7 to 9, respectively. Specifically, Fig. 7 is a graph showing the discharge of the cell subjected to 1.5 A pulses
30 wherein curve 70 was constructed from the prepulse voltage and curves 72 and 74 were constructed from the P1 Min. and P4 Min. discharge voltages versus delivered capacity, respectively. Fig. 8 is a graph showing the discharge of the cell subjected to 1.75 A pulses wherein
35 curve 80 was constructed from the prepulse voltage and curves 82 and 84 were constructed from the P1 Min. and

- 20 -

P4 Min. discharge voltages versus delivered capacity, respectively. Finally, Fig. 9 is a graph showing the discharge of the cell subjected to the 2.0 A pulses wherein curve 90 was constructed from the prepulse
5 voltage and curves 92 and 94 were constructed from the P1 Min. and P4 Min. discharge voltages versus delivered capacity, respectively.

Table 3 shows the capacity delivered by each cell to the specified cutoffs:

10

TABLE 3

| | Ah to 2 V | Ah to 1.7 V | Ah to 1.5 V |
|---------------|-----------|-------------|-------------|
| 1.5 A trains | 280 | 377 | 426 |
| 1.75 A trains | 247 | 359 | 410 |
| 15 2 A trains | 228 | 339 | 392 |

It was shown that cathodes prepared according to the present invention from a slurry of an electrode active material, exemplified by silver vanadium oxide,
20 contacted to a surface-treated foil collector can be wound about a 1/8 inch metal rod while maintaining their mechanical integrity, even after several windings and unwindings. Thus, the electrodes comprising a cathode active material contacted to a surface treated
25 conductive foil according to the present invention exhibit improved structural integrity even when tightly wound with an anode in a jellyroll configuration while maintaining high current densities typically associated with an alkali metal/mixed metal oxide electrical
30 couple. It is noted that dry cathode active materials pressed to untreated conductive substrates according to the prior art have been known to experience noticeable separation or sloughing off from the current collector during manufacture, particularly while being wound with
35 the anode into the jellyroll configuration. While acceptable, the etched surface of the conductive foil

according to the present invention helps prevent even slight separation or sloughing from occurring without deterring from the energy density of the cell. In fact, cells incorporating electrodes fabricated according to
5 the present invention having thickness in the range of about 0.002 to about 0.009 inches exhibit comparable to increased discharge capacities with respect to prior art cells of similar chemistries. It is believed that the increased capacity is at least partially attributable to
10 increased contact surface area between the electrode active material and the current collector.

EXAMPLE V

15

Silver vanadium oxide was sieved to less than 140 mesh and, 4.25 grams of the sieved material was combined with 10 grams of graphite #38 and 15 grams of Ketjenblack carbon using a mortar and pestle. The
20 resulting mixture was added to a solution of 50 grams Kynar 461 polyvinylidene fluoride in 800 grams of dimethyl formamide and 10 grams of propylene carbonate. The resulting slurry was milled/mixed and transferred to untreated Reynolds, heavy duty aluminum foil of 0.001
25 inches in thickness using a scoopula. The slurry was spread using a doctor blade with a gap of 0.015 inches such that a uniform coating resulted. The casting was allowed to dry to a thickness of about 0.008 inches in a heated chamber before a coupon of 5.2 cm² was cut from
30 the laminate. A 0.125 x 0.125 inch area was cleared from one corner of the coupon before it was pressed at 6.15 tons/cm² to provide the coupon having an active material thickness of about 0.004 inches. A 0.125 x 6 inch aluminum lead was resistance spot welded to the
35 cleared area of the cathode active coupon laminate.

The cathode laminate was wrapped in two layers of CELGARD 4560 polypropylene separator material, and a coupon of lithium metal of the same dimension was placed against the SVO coated side of the cathode as was a
5 screen with a lead to serve as a current collector for the lithium anode. The electrode assembly was held together using a metal clip and positioned in a glass vessel of suitable dimension with the leads allowed to hang over the rim of the vessel. The vessel was filled
10 by 1M LiAsF₆ in 1:1, by volume, propylene carbonate and 1,2-dimethoxyethane. A rubber stopper provided a lid for the vessel.

The cell was discharged using semi-hourly applied pulse trains comprising four, 10 second, 0.094 A
15 (0.018A/cm²) pulses with 15 seconds rest between each pulse. A plot of the discharge curves are present in Fig. 10. Specifically, curve 100 was constructed from the prepulse voltage of the cell constructed according to this example, and curves 102 and 104 were constructed
20 from the P1 Min. and P4 Min. discharge voltages versus delivered capacity, respectively of this cell. The cell delivered 0.0075 Ah to a 2 V cutoff as defined by a pulse minimum at or below 2 V.

The mechanical integrity of the coupon laminates
25 was tested by manipulating them into the S-shaped configuration described in Example II. It was noted that even with an untreated foil, the cast and pressed active mixture did not exhibit mechanical failure as no sloughing off or crack of the active material was noted.
30 Furthermore, it was an unexpected advantage of the present invention that the application of a slurry of cathode active material to a cleaned but untreated conductive substrate had sufficient mechanical integrity for incorporation into a cell while exhibiting
35 comparable to increased discharge capacities with

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respect to capacities known for prior art press powder cells.

It is appreciated that various modifications to the inventive concepts described herein may be apparent to those skilled in the art without departing from the spirit and the scope of the present invention defined by the hereinafter appended claims.

What is claimed is:

1. An electrochemical cell, which comprises:
 - a) an anode;
 - b) a cathode characterized as having been formed from a slurry comprising a cathode active material mixed with a solvent material and contacted to a current collector, and after removal of the solvent material, calendared to the current collector; and
 - c) an electrolyte solution operatively associated with the anode and the cathode.
2. The electrochemical cell of claim 1 wherein the current collector comprises a metal selected from the group consisting of aluminum, nickel, titanium, mild steel and stainless steel, and mixtures thereof.
3. The electrochemical cell of claim 1 wherein the cathode is characterized as being flexible.
4. The electrochemical cell of claim 1 wherein the cathode has a thickness ranging from about 0.002 inches to about 0.009 inches.
5. The electrochemical cell of claim 1 wherein the casing comprises a metal selected from the group consisting of titanium, stainless steel, mild steel, nickel-plated mild steel and aluminum.
- 30 6. An electrochemical cell comprises:
 - (a) an anode;
 - (b) a cathode comprising a cathode active material contacted to a surface treated current collector, the current collector being surface treated to increase the surface area contacted by the cathode active material; and

- 25 -

(c) an electrolyte solution operatively associated with the anode and the cathode.

7. The electrochemical cell of claim 6 wherein the
5 current collector comprises a metal selected from the group consisting of aluminum, nickel, titanium, mild steel and stainless steel, and mixtures thereof.

8. The electrochemical cell of claim 6 wherein the
10 current collector is characterized as having been etched by contacting with an acid solution prior to being contacted with the cathode active material.

9. The electrochemical cell of claim 6 wherein the
15 cathode is characterized as being flexible.

10. The electrochemical cell of claim 6 wherein the cathode has a thickness ranging from about 0.002 inches to about 0.009 inches.

20

11. An electrochemical cell comprises:

(a) an anode;
(b) a cathode characterized as having been formed from a slurry comprising a cathode active material mixed
25 with a solvent material and contacted to a current collector, and after removal of the solvent material, calendared to the current collector, wherein the cathode active material is selected from the group consisting of a metal, a metal oxide, a mixed metal oxide and a metal sulfide, and mixtures thereof; and

(c) an electrolyte solution operatively associated with the anode and the cathode.

12. The electrochemical cell of claim 11 wherein the
35 current collector is characterized as having been

treated to increase the surface area thereof contacted by the cathode active material.

13. The electrochemical cell of claim 11 wherein the
5 current collector is treated by contact with an acid
solution.

14. The electrochemical cell of claim 13 wherein the
current collector is characterized as having been
10 contacted by a sulfuric acid solution for about 8 to 12
minutes at about 50°C to 70°C.

15. The electrochemical cell of claim 11 wherein the
current collector is untreated prior to contact with the
15 cathode active material.

16. The electrochemical cell of claim 11 wherein the
current collector comprises a metal selected from the
group consisting of aluminum, nickel, titanium and
20 stainless steel, and mixtures thereof.

17. The electrochemical cell of claim 11 wherein the
metal oxide or the mixed metal oxide of the cathode
active material is formed as a preparation product of
25 one of the group consisting of a thermal treatment
reaction, addition reaction, sol-gel formation, chemical
vapor deposition and hydrothermal synthesis of vanadium
oxide and at least a second metal.

30 18. The electrochemical cell of claim 11 wherein the
cathode active material is selected from the group
consisting of silver vanadium oxide, copper silver
vanadium oxide, manganese dioxide, lithium cobalt oxide,
lithium nickel oxide, copper oxide, titanium disulfide,
35 copper sulfide, iron sulfide, iron disulfide, copper
vanadium oxide, and mixtures thereof.

19. The electrochemical cell of claim 11 wherein the cathode comprises either silver vanadium oxide or copper silver vanadium oxide contacted to the current collector, and wherein the current collector comprises aluminum.

5 20. The electrochemical cell of claim 11 wherein the cathode active material is mixed with at least one of a binder material and a conductive additive.

10

21. The electrochemical cell of claim 20 wherein the binder material is a fluoro-resin powder.

15

22. The electrochemical cell of claim 20 wherein the conductive additive is selected from the group consisting of carbon, graphite power, acetylene black and metallic powder selected from the group consisting of titanium, aluminum, nickel and stainless steel, mixtures thereof.

20

23. The electrochemical cell of claim 20 wherein the conductive additive is Ketjenblack carbon.

25

24. The electrochemical cell of claim 20 wherein the cathode comprises up to about 5 weight percent conductive additive and about 1 to 10 weight percent of the binder material.

30

25. The electrochemical cell of claim 11 where the cathode comprises, by weight, about 94% silver vanadium oxide, about 3% of a fluoro-resin powder and about 3% Ketjenblack carbon.

35

26. The electrochemical cell of claim 11 wherein the anode is comprised of lithium.

27. The electrochemical cell of claim 11 wherein the anode comprises a lithium-aluminum alloy.

28. The electrochemical cell of claim 11 wherein the
5 electrolyte solution operatively associated with the anode and the cathode comprises an ion-forming alkali metal salt dissolved in a nonaqueous solvent, and wherein the alkali metal of the salt is similar to the alkali metal comprising the anode.

10

29. The electrochemical cell of claim 28 wherein the alkali metal of the anode comprises lithium and the ion-forming alkali metal salt comprising the electrolyte solution is selected from the group consisting of LiPF₆,
15 LiAsF₆, LiSbF₆, LiBF₄, LiClO₄, LiAlCl₄, LiGaCl₄, LiC(SO₂CF₃)₃, LiN(SO₂CF₃)₂, LiSO₃F, LiB(C₆H₅)₄ and LiCF₃SO₃, and mixtures thereof.

30. The electrochemical cell of claim 28 wherein the
20 nonaqueous solvent comprises at least one organic solvent selected from the group consisting of tetrahydrofuran, propylene carbonate, methyl acetate, acetonitrile, dimethyl sulfoxide, dimethyl formamide, dimethyl acetamide, ethylene carbonate, diglyme,
25 triglyme, tetraglyme, 1,2-dimethoxyethane, dimethyl carbonate, diethyl carbonate, γ -butyrolactone and N-methyl-pyrrolidinone, and mixtures thereof.

31. The electrochemical cell of claim 11 wherein the
30 nonaqueous solvent is an organic solvent that comprises propylene carbonate and dimethoxyethane.

32. The electrochemical cell of claim 31 wherein the
propylene carbonate and dimethoxyethane are present in a
35 ratio of about 1:1 by volume.

33. The electrochemical cell of claim 11 wherein the cathode is characterized as being flexible.

5 34. The electrochemical cell of claim 11 wherein the cathode has a thickness ranging from about 0.002 inches to about 0.009 inches.

10 35. An electrochemical cell, which comprises:

a) an anode comprising an alkali metal;

b) a cathode characterized as having been formed from a slurry including a mixed metal oxide mixed with a solvent material and contacted to a current collector, and after removal of the solvent material, calendered to the current collector, wherein the mixed metal oxide is comprised of vanadium oxide and a second metal "SM" selected from the group consisting of Groups IB, IIB, IIIB, IVB, VIB, VIIIB and VIII of the Periodic Table of the Elements, the mixed oxide matrix having the general formula $SM_xV_2O_y$, wherein $0.30 \leq x \leq 2.0$ and $4.5 \leq y \leq 6.0$;

15 and

c) an electrolyte solution operatively associated with the anode and the cathode.

20 36. The electrochemical cell of claim 35 wherein the current collector comprises a metal selected from the group consisting of aluminum, nickel, titanium, metal steel and stainless steel and mixtures thereof.

25 37. The electrochemical cell of claim 35 wherein the current collector is characterized as having been treated to increase the surface area thereof contacted by the cathode active material.

30 38. The electrochemical cell of claim 37 wherein the current collector is characterized as having been contacted by an acid solution.

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39. The electrochemical cell of claim 35 wherein the current collector is untreated prior to contact with the cathode active material.

5 40. The electrochemical cell of claim 35 wherein the second metal is a silver compound selected from the group consisting of silver nitrate, silver nitrite, silver carbonate, and salts of silver oxyanions.

10 41. The electrochemical cell of claim 35 wherein the mixed metal oxide is formed as a preparation product of one of the group consisting of a thermal treatment, sol-gel formation, chemical vapor deposition and hydrothermal synthesis of vanadium oxide and the second metal.

15 42. The electrochemical cell of claim 35 wherein the cathode is characterized as being flexible.

20 43. The electrochemical cell of claim 35 wherein the cathode has a thickness ranging from about 0.002 inches to about 0.009 inches.

25 44. An electrochemical cell, which comprises:

a) an anode;

b) a cathode characterized as having been formed from a slurry including a mixed metal oxide mixed with a solvent material and contacted to a current collector, and after removal of the solvent material, calendared to 30 the current collector, wherein the mixed metal oxide comprises vanadium oxide and a mixture of copper and a second metal "SM" selected from the group consisting of Groups IB, IIB, IIIB, IVB, VIB, VIIIB, and VIII of the Periodic Table of the Elements, the mixed oxide matrix 35 having the general formula $Cu_xSM_yV_zO$, wherein $0.01 \leq x \leq 1.0$, $0.01 \leq y \leq 1.0$ and $5.01 \leq z \leq 6.5$; and

c) an electrolyte solution operatively associated with the anode and the cathode.

45. The electrochemical cell of claim 44 wherein in the
5 general formula $x \leq y$.

46. The electrochemical cell of claim 44 wherein one component of the cathode comprises copper-silver-vanadium oxide as the mixed metal oxide.

10

47. The electrochemical cell of claim 44 wherein the current collector comprises a metal selected from the group consisting of aluminum, nickel, titanium and stainless steel and mixtures thereof.

15

48. The electrochemical cell of claim 44 wherein the current collector is characterized as having been treated to increase the surface area thereof contacted by the cathode active material.

20

49. The electrochemical cell of claim 48 wherein the current collector is characterized as having been contacted by an acid solution.

25

50. The electrochemical cell of claim 44 wherein the cathode is characterized as being flexible.

30

51. The electrochemical cell of claim 44 wherein the cathode has a thickness ranging from about 0.002 inches to about 0.009 inches.

35

52. An electrode for an electrochemical cell, the electrode characterized as having been formed from a slurry comprising a mixed metal oxide mixed with a solvent material and contacted to a current collector, and after removal of the solvent material, calendered to

the current collector, wherein the mixed metal oxide comprises vanadium oxide and a second material "SM" selected from the group consisting of Groups IB, IIB, IIB, IVB, VIB, VIIIB and VIII of the Periodic Table of 5 the Elements, the mixed metal oxide having the general formula $SM_xV_2O_y$, wherein $0.30 \leq x \leq 2.0$ and $4.5 \leq y \leq 6.0$.

53. The electrode of claim 52 wherein the current collector is characterized as having been treated to 10 increase the surface area contacted by the mixed metal oxide.

54. The electrode of claim 53 wherein the current collector is characterized as having been contacted by 15 an acid solution.

55. The electrode of claim 52 wherein the current collector comprises a metal selected from the group consisting of aluminum, nickel, titanium, mild steel and 20 stainless steel, and mixtures thereof.

56. The electrode of claim 52 wherein the second metal is included in a compound selected from the group consisting of a metal nitrate, a metal nitrite, a metal 25 carbonate and ammonium salts of transition metal oxyanions.

57. The electrode of claim 52 characterized as being flexible.

30 58. The electrode of claim 52 wherein the cathode has a thickness ranging from about 0.002 inches to about 0.009 inches.

35 59. A electrode for an electrochemical cell, the electrode characterized as having been formed from a

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slurry comprising a mixed metal oxide mixed with a solvent material and contacted to a current collector, and after removed of the solvent material, calendered to the current collector, wherein the mixed metal oxide
5 comprises a mixture of vanadium oxide and copper and a second metal "SM" selected from the group consisting of Groups IB, IIB, IIIB, IVB, VIB, VIIIB, and VIII of the Periodic Table of the Elements, the mixed metal oxide having the general formula $Cu_xSM_yV_zO$, wherein $0.01 \leq x \leq 1.0$, $0.01 \leq y \leq 1.0$ and $5.01 \leq z \leq 6.5$.
10

60. The electrode of claim 59 wherein in the general formula $x \leq y$.

15 61. The electrode of claim 59 wherein the current collector comprises a metal selected from the group consisting of aluminum, nickel, titanium, mild steel and stainless steel and mixtures thereof.

20 62. The electrode of claim 59 wherein the current collector is characterized as having been treated to increase the surface area contacted by the mixed metal oxide.

25 63. The electrode of claim 62 wherein the current collector is characterized as having been contacted by an acid solution.

30 64. The electrode of claim 59 characterized as being flexible.

65. The electrode of claim 59 wherein the cathode has a thickness ranging from about 0.002 inches to about 0.009 inches.

66. A method of providing an electrochemical cell, which comprises:

- a) providing a casing;
- b) housing an electrochemical cell within
5 the casing, comprising the steps of:
 - i) providing an anode;
 - ii) providing a cathode, comprising the steps of:
 - mixing a cathode active material with a
10 solvent material to form a slurry;
 - contacting the slurry comprising the cathode active material to the current collector; removing the solvent material from the cathode active material; and
 - pressing the cathode active material to
15 the current collector; and
 - iii) positioning the anode and the cathode inside the casing; and
 - c) activating the anode and the cathode with
20 an electrolyte solution filled in the casing.

67. The method of claim 66 including treating the conductive current collector to increase the surface area thereof.

- 25
68. The method of claim 66 including selecting the cathode active material from the group consisting of a metal, a metal oxide, a mixed metal oxide and a metal sulfide, and mixtures thereof.

- 30
69. The method of claim 66 including selecting the current collector from the group consisting of aluminum, nickel, titanium, mild steel and stainless steel, and mixtures thereof.

70. A method of providing an electrochemical cell, which comprises:

- (a) providing a casing;
- (b) housing an electrochemical cell within the
5 casing, comprising the steps of:
 - i) providing an anode;
 - ii) providing a cathode, comprising the steps
of: providing a cathode active material
selected from the group consisting of a
metal, a metal oxide, a mixed metal oxide
and a metal sulfide, and mixtures
thereof;
 - treating a conductive current
collector to increase the surface area
15 thereof; and
 - contacting the cathode active
material to the surface treated current
collector; and
 - iii) positioning the anode and the cathode
20 inside the casing; and
- (c) activating the anode and the cathode with an
electrolyte solution filled in the casing.

25 71. The method of claim 70 including the selecting the
current collector from the group consisting of aluminum,
nickel, titanium and stainless steel, and mixtures
thereof.

30 72. The method of claim 70 including contacting the
current collector with an acid solution.

73. The method of claim 72 wherein the acid solution
comprises sulfuric acid.

74. The method of claim 73 including contacting the current collector with the sulfuric acid solution for about 8 to 12 minutes at about 50°C to 70°C.

5 75. The method of claim 70 including selecting the cathode active material from the group consisting of silver vanadium oxide, copper silver vanadium oxide, manganese dioxide, lithium cobalt oxide, lithium nickel oxide, copper oxide, titanium disulfide, copper sulfide, iron 10 sulfide, iron disulfide, copper vanadium oxide, and mixtures thereof.

76. The method of claim 70 including providing the anode comprised of lithium.

15 77. The method of claim 70 including providing the electrolyte solution operatively associated with the anode and the cathode comprising an ion-forming alkali metal salt dissolved in a nonaqueous solvent, and 20 wherein the alkali metal of the salt is similar to the alkali metal comprising the anode.

78. The method of claim 70 including providing the alkali metal of the anode comprising lithium and 25 selecting the ion-forming alkali metal salt comprising the electrolyte solution from the group consisting of LiPF₆, LiAsF₆, LiSbF₆, LiBF₄, LiClO₄, LiAlCl₄, LiGaCl₄, Li(SO₂CF₃)₃, LiN(SO₂CF₃)₂, LiSO₃F, LiB(C₆H₅)₄ and LiCF₃SO₃, and mixtures thereof.

30 79. The method of claim 77 including providing the nonaqueous solvent comprising an organic solvent selected from the group consisting of tetrahydrofuran, propylene carbonate, dimethyl carbonate, diethyl 35 carbonate, methyl acetate, acetonitrile, dimethyl sulfoxide, dimethyl formamide, dimethyl acetamide,

γ -butyrolactone, N-methyl-pyrrolidinone, ethylene carbonate, diglyme, triglyme, tetraglyme, 1,2-dimethoxyethane and mixtures thereof.

5 80. The method of claim 70 wherein the step of contacting the cathode active material to the surface treated current collector includes forming a slurry comprising the cathode active material and a solvent, and applying the slurry to the current collector.

10

81. A method of providing an electrode, comprising the steps of:

- a) mixing an electrode active material with a solvent material to form a slurry;
- 15 b) contacting the slurry comprising the electrode active material to the current collector;
- c) removing the solvent material from the electrode active material; and
- 20 d) pressing the electrode active material to the current collector.

25 82. The method of claim 81 including treating the conductive current collector to increase the surface area thereof prior to contacting the slurry to the current collector.

30 83. The method of claim 81 including selecting the electrode active material from the group consisting of a metal, a metal oxide, a mixed metal oxide and a metal sulfide, and mixtures thereof.

35 84. The method of claim 81 including selecting the current collector from the group consisting of aluminum, nickel, titanium, mild steel and stainless steel, and mixtures thereof.

85. The method of claim 83 including selecting the cathode active material from the group consisting of silver vanadium oxide, copper silver vanadium oxide, manganese dioxide, lithium cobalt oxide, lithium nickel oxide, copper oxide, titanium disulfide, copper sulfide, iron sulfide, iron disulfide, copper vanadium oxide, and mixtures thereof.

5
10 86. A method of providing an electrode, comprising the steps of:

- a) providing an electrode active material selected from the group consisting of a metal, a metal oxide, a mixed metal oxide and a metal sulfide, and mixtures thereof;
- b) treating a conductive current collector to increase the surface area thereof; and
- c) contacting the electrode active material to the surface treated current collector.

15
20 87. The method of claim 86 including selecting the current collector from the group consisting of aluminum, nickel, titanium, mild steel and stainless steel, and mixtures thereof.

25 88. The method of claim 86 including contacting the current collector with an acid solution.

30
35 89. The method of claim 86 including selecting the electrode active material from the group consisting of silver vanadium oxide, copper silver vanadium oxide, manganese dioxide, lithium cobalt oxide, lithium nickel oxide, copper oxide, titanium disulfide, copper sulfide, iron sulfide, iron disulfide, copper vanadium oxide, and mixtures thereof.

90. The material of claim 86 wherein the step of contacting the electrode active material to the surface treated current collector includes forming a slurry comprising the electrode active material and a solvent
5 and, applying the slurry to the current collector.

91. A substrate which comprises a sheet of electrically conductive material characterized as having been
10 contacted by an acid solution to increase the surface area thereof.

92. The substrate of claim 91 wherein the electrically conductive material is selected from the group
15 consisting of aluminum, nickel, titanium, mild steel and stainless steel, and mixtures thereof.

93. The substrate of claim 91 wherein the acid solution comprises sulfuric acid.

20
94. The substrate of claim 93 wherein the electrically conductive material is characterized as having been contacted by the sulfuric acid solution for about 8 to 12 minutes at about 50°C to 70°C.

25
95. A method of making a thin flexible cathode for use in an electrochemical cell comprising the steps of:
a) providing a metal foil cathode current collector;
30 b) providing a slurry of cathode active material comprising silver vanadium oxide, organic binder material and carbon material mixed together in a solvent material;
c) casting the slurry to the treated surface of
35 the cathode current collector;

- 40 -

- d) removing the solvent material from the cathode active material; and
- e) pressing the resulting laminate to provide a thin flexible cathode.

5

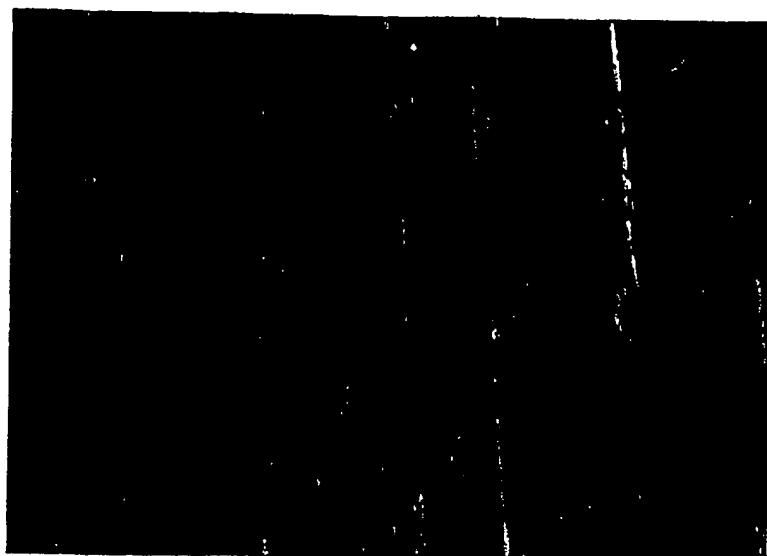
96. The method of claim 95 including treating a surface of the current collector to increase the operative surface area thereof prior to contacting the slurry to the current collector.

10

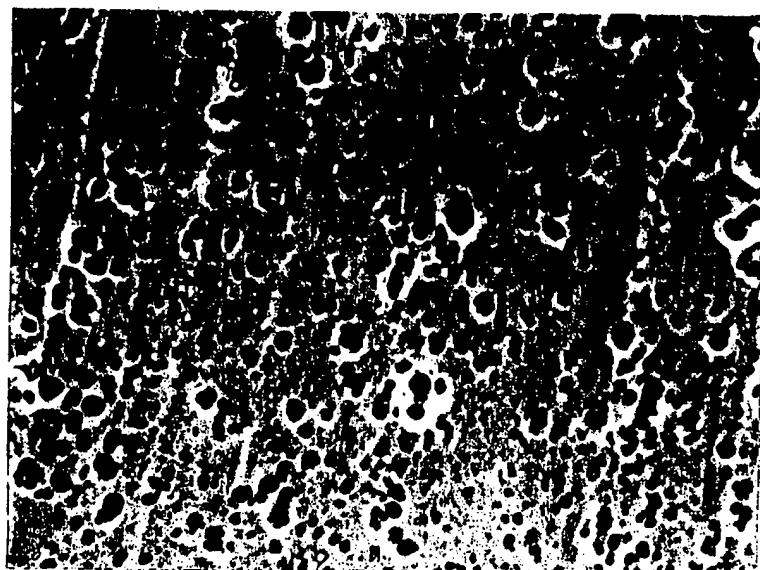
97. The method of claim 96 including treating the surface of the cathode current collector by contacting with an acid solution.

15

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—FIG. 1



—FIG. 2

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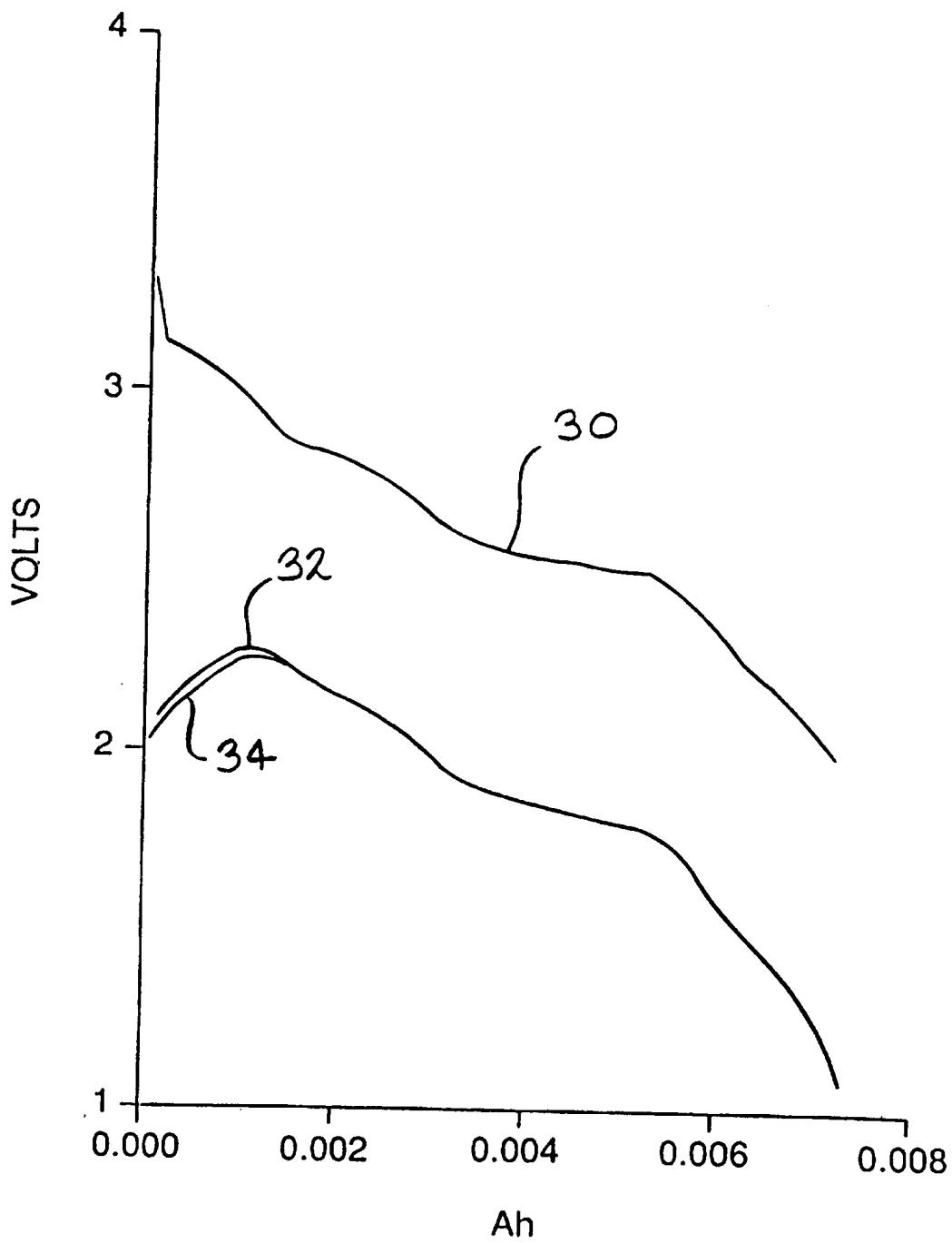


FIG. 3

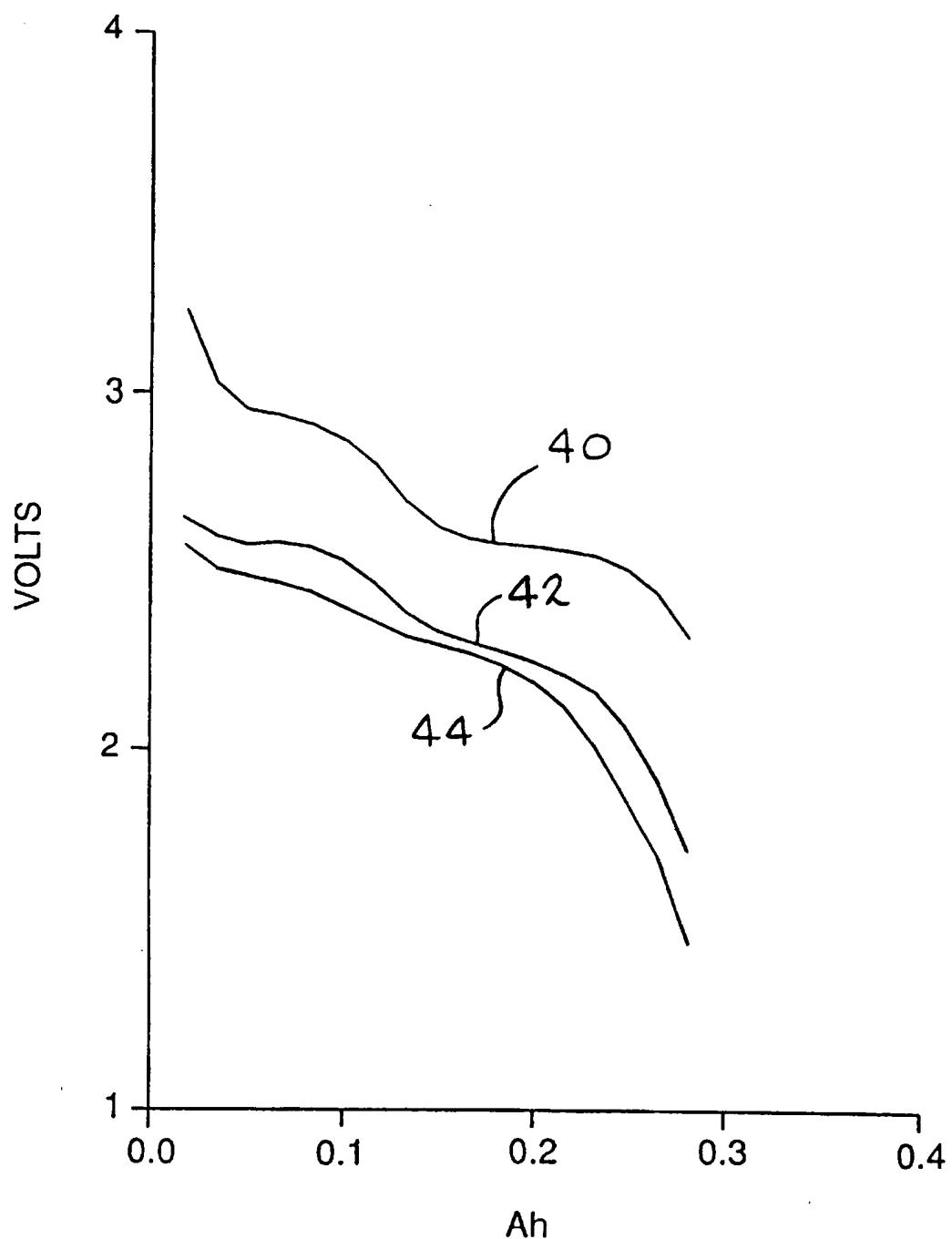
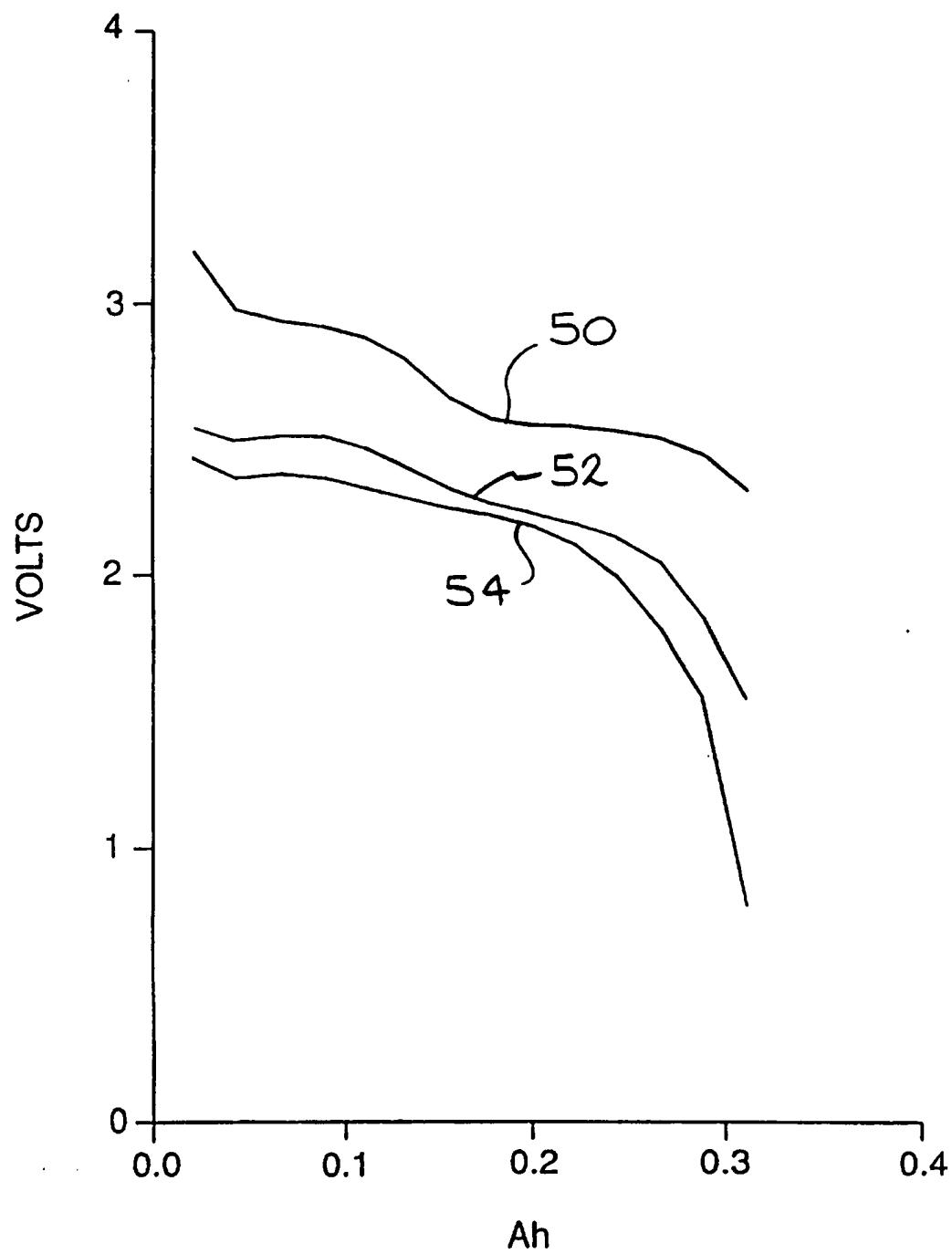
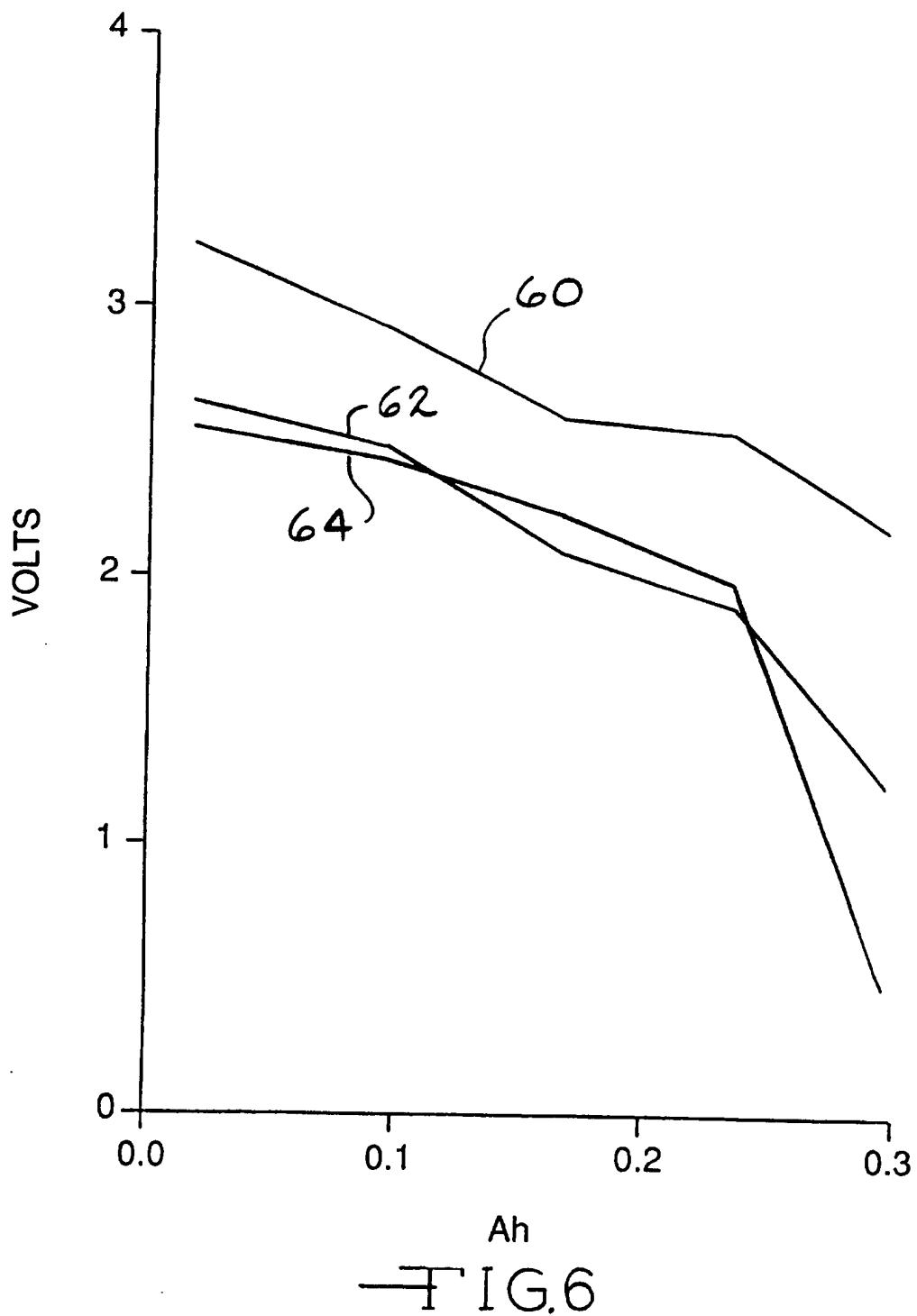


FIG. 4

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—FIG. 5



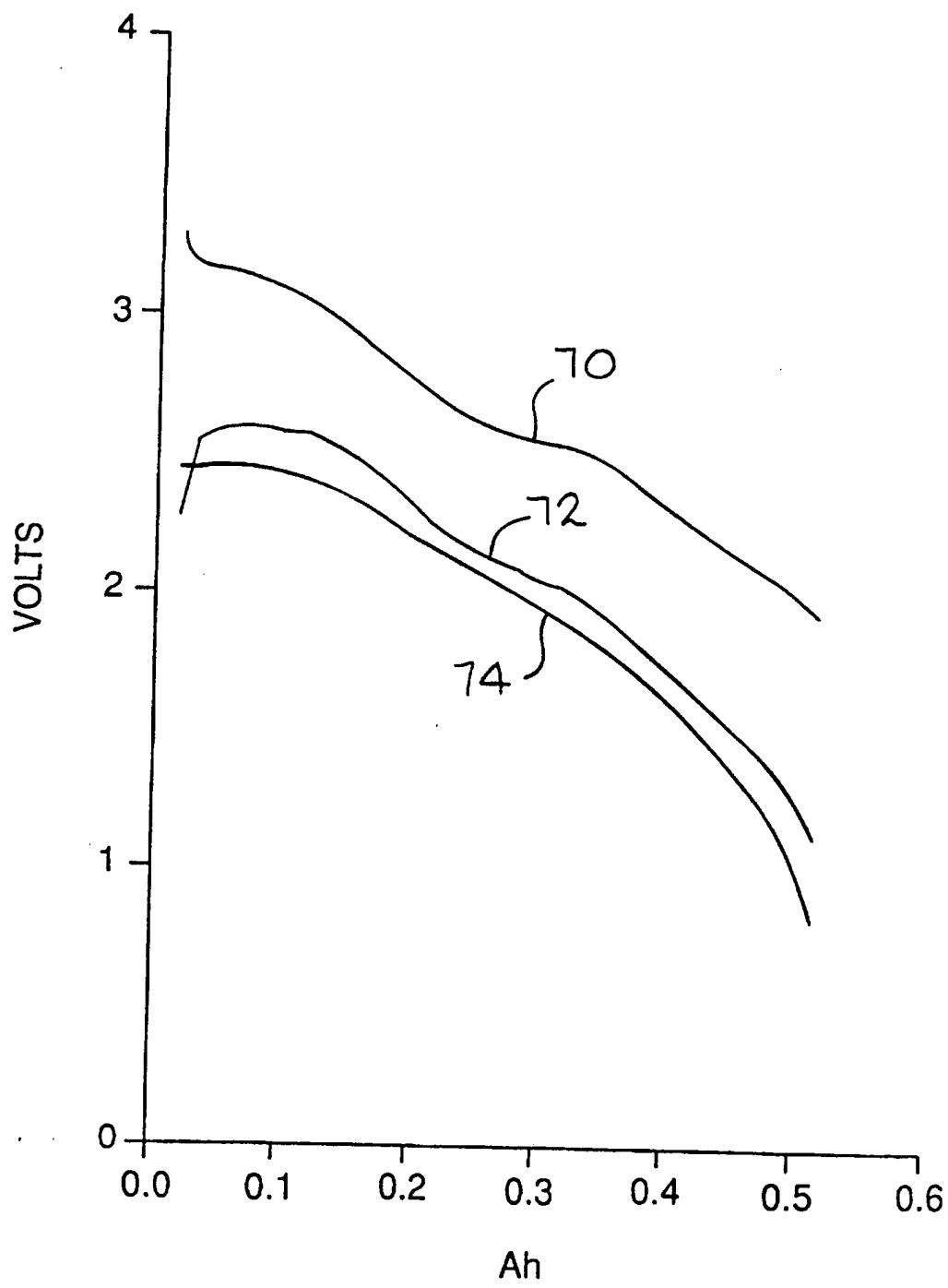


FIG. 7

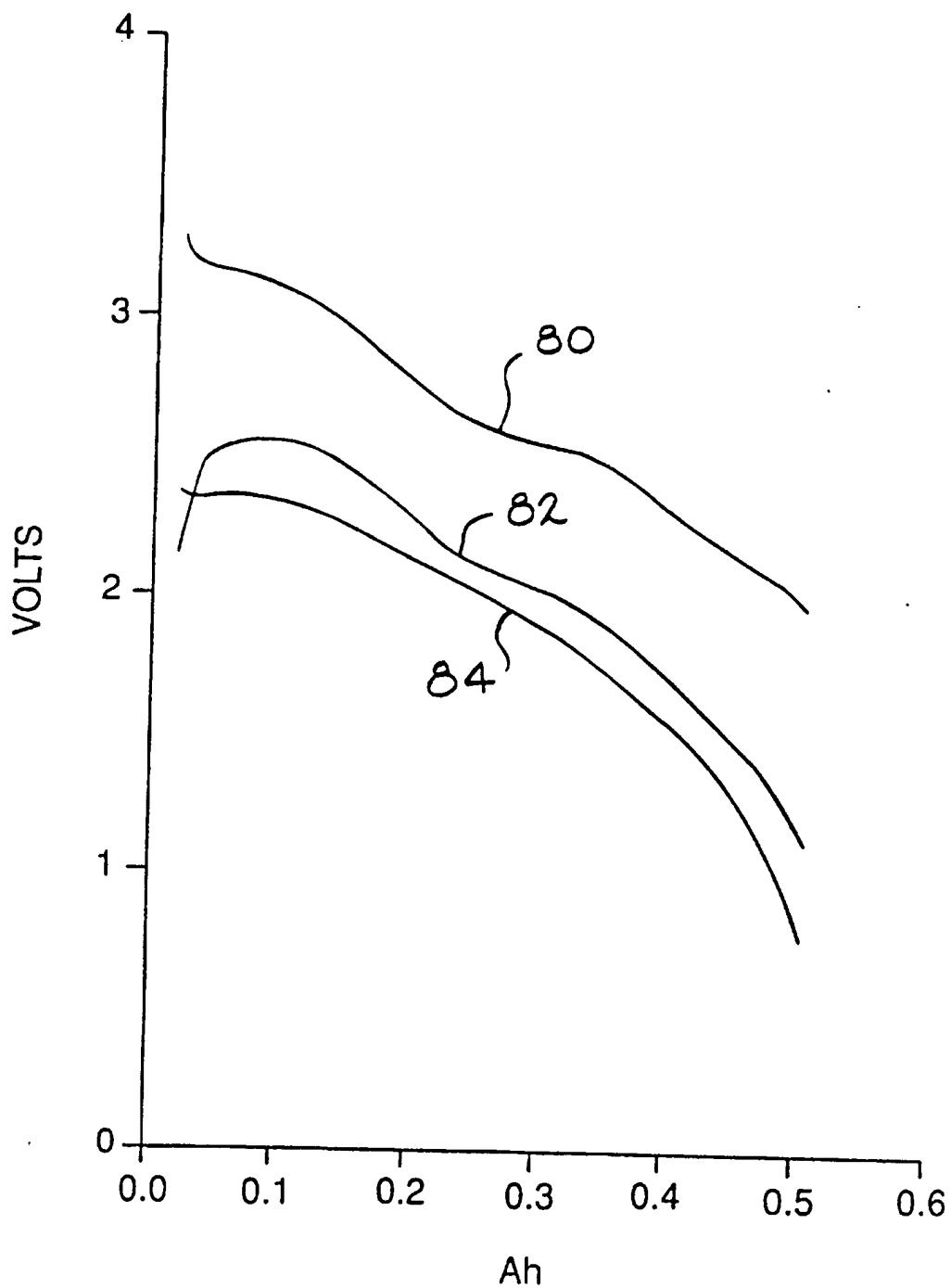


FIG. 8

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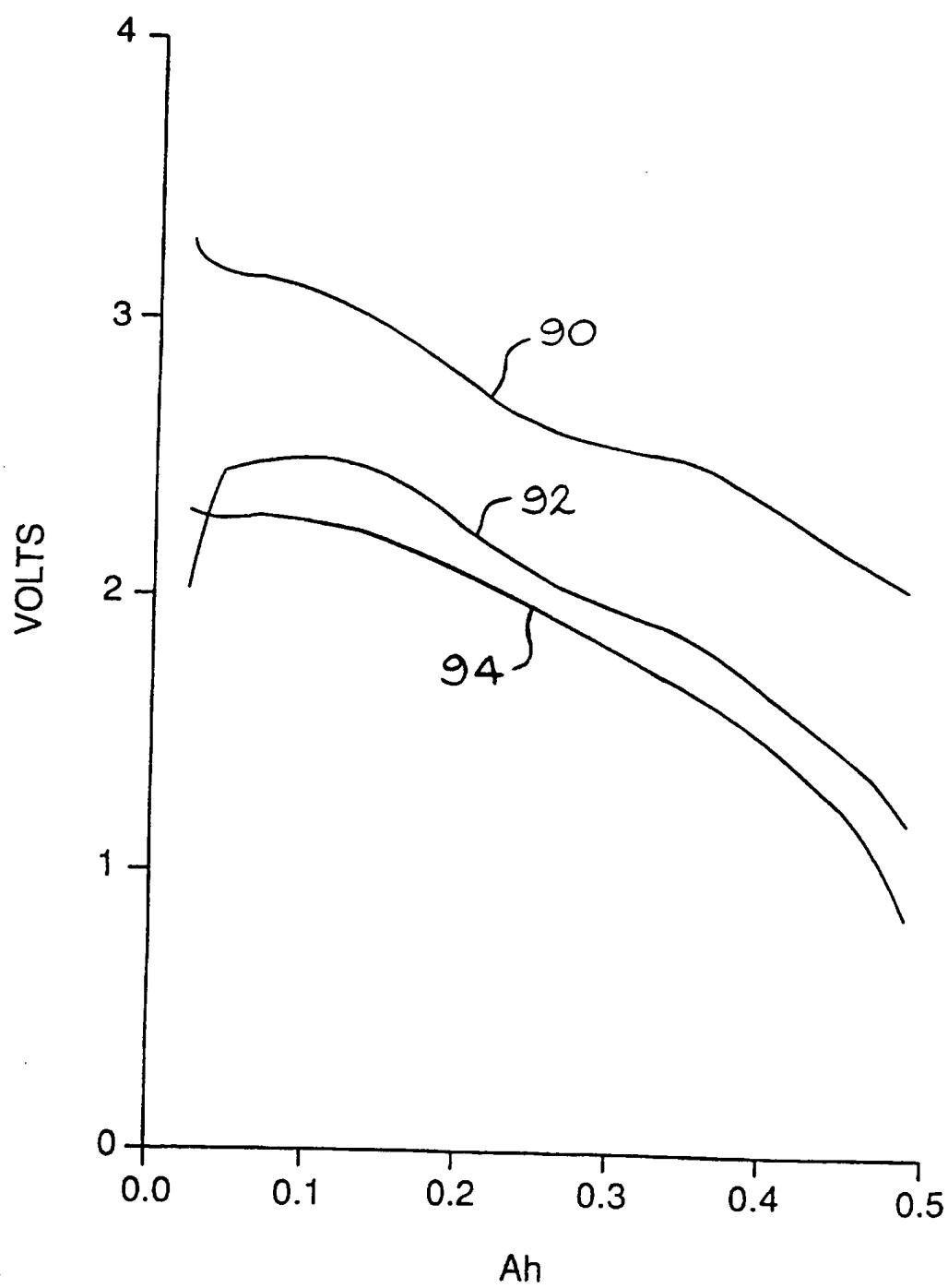


FIG. 9

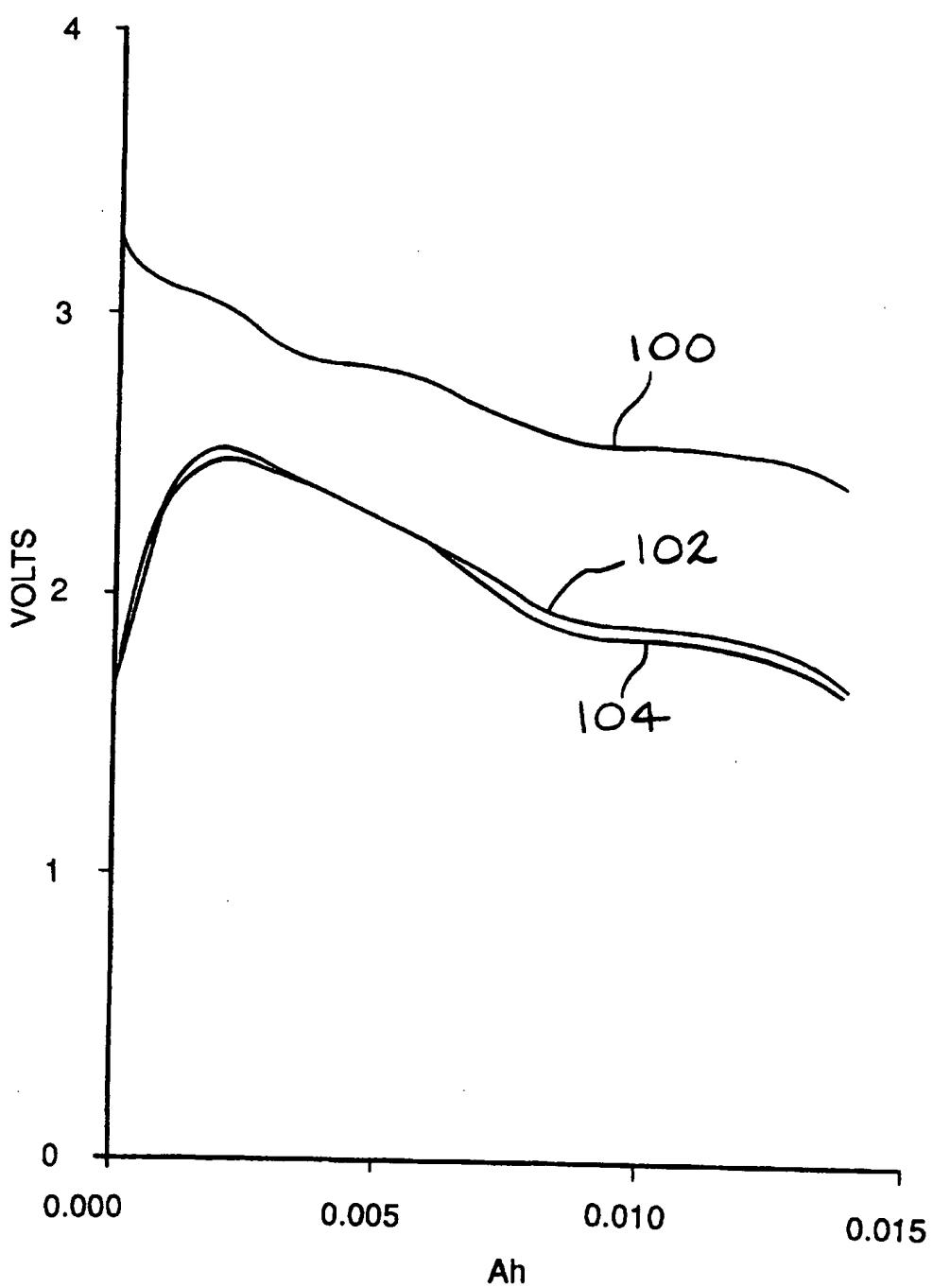
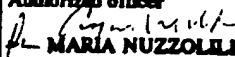


FIG 10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/04975

| A. CLASSIFICATION OF SUBJECT MATTER | | |
|--|---|--|
| IPC(6) :H01M 6/14, 6/18, 4/60 US CL :429/194,197,218, 220, 233, 247 According to International Patent Classification (IPC) or to both national classification and IPC | | |
| B. FIELDS SEARCHED | | |
| Minimum documentation searched (classification system followed by classification symbols) U.S. : 429/194,197,218, 220, 233, 247 | | |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched NONE | | |
| Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) APS, STN search terms: current collector, etched, stainless steel, aluminum, battery, | | |
| C. DOCUMENTS CONSIDERED TO BE RELEVANT | | |
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| X - Y | US 5,424,151 A (KOKSBANG ET AL.) 13 June 1995, col. 5, lines 58-68, col. 6, lines 1-3, lines 14-30, col. 10, lines 30-68 | 1-17 ----- 20-30 |
| Y, P | US 5,580,683 A (TAKEUCHI ET AL.) 03 DEC 1996, col. 5, lines 40-67, col. 6, lines 1-5, lines 20-49, col. 9, lines 30-43, col. 10, lines 45-68 | 1-97 |
| Y, E | US 5,616,366 A (OLSEN ET A.) 01 April 1997, col. 5, lines 50-62, col. 6, lines 10-46 | 1-97 |
| Y | US 5,436,091 A (SHACKLE ET AL.) 25 July 1995, col.4, lines 41-68, col. 5, lines 1-45, col. 6, lines 59-68 | 1-97 |
| <input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex. | | |
| <ul style="list-style-type: none"> * Special categories of cited documents: *'A' document defining the general state of the art which is not considered to be of particular relevance *'B' earlier document published on or after the international filing date *'L' document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reasons (as specified) *'O' document referring to an oral disclosure, use, exhibition or other means *'P' document published prior to the international filing date but later than the priority date claimed | | <small>*'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</small> <small>*'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</small> <small>*'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</small> <small>*'Z' document number of the same patent family</small> |
| Date of the actual completion of the international search 11 MAY 1997 | Date of mailing of the international search report 09 JUL 1997 | |
| Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230 | Authorized officer  MARIA NUZZOLILLO Telephone No. (703) 308-0661 | |